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TECHNICAL INFORMATION SERIES

R61SD147

THE MEASUREMENT OF VAPOR PRESSURE OF ATOMIC SPECIES FROM SPECTROPHOTOMETRIC MEASUREMENTS OF THE ABSORPTION OF RESONANCE LINES

V. THE FREE ENERGY OF FORMATION OF TiC AND ZrC

G. L. VIDALE

SPACE SCIENCES LABORATORY
GENERAL ELECTRIC
MISSILE AND SPACE VEHICLE DEPARTMENT

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SPACE SCIENCES LABORATORY

AEROPHYSICS OPERATION

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V. The Free Energy of Formation of TiC and ZrC*

By

G. L. Vidale

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GENERAL ELECTRIC

ABSTRACT

Spectrophotometric measurements of the absorption of the Ti_{3371} and the Zr_{3601} resonance lines were made of the equilibrium vapor over the pure metals and over the corresponding carbides, utilizing a hollow cathode discharge tube source previously described to generate the thin resonance lines. From the ratio of the pressure of the metal atoms over the pure metal, and over TiC and ZrC, the standard free energy of formation of each carbide has been computed. The corresponding values of the standard heat of formation were then obtained with the aid of the known entropies and heats of warming of the various compounds.

It was found that for TiC

$$\Delta F^{o}_{f_{2220}} = -35.5 \pm .5 \text{ kcal/mole}$$

$$\Delta H^{o}_{f_{298}} = -42.7 \pm .5 \text{ kcal/mole}$$

and for ZrC

$$\Delta F^{o}_{f_{2740}} = -38.8 \pm 1 \text{ kcal/mole}$$

and $\Delta H^{o}_{f_{298}} = -47.6 \pm 3$ kcal/mole

CONTENTS

I. INTRODUCTION

The purpose of this investigation was the measurement of the standard molar free energy of formation of $TiC_{(s)}$ and $ZrC_{(s)}$.

In an earlier report[1], the best thermodynamic data available for the two compounds was listed and used for predicting the free energy of formation of these compounds at elevated temperatures. Some of the quantities used were seen to have relatively large probable errors. Also, extrapolations of doubtful accuracy were needed in order to determine the value of ΔH and ΔS of formation of the compounds at temperatures higher than 1500°K.

The conclusion was that the resulting vapor pressure values so obtained were most uncertain for ZrC, and needed experimental confirmation for TiC.

The experimental method and equipment used here are the same as were used in the analogous study of the free energy of formation of silicon carbide, which has been described in detail in a previous report[2]. The experiment consisted of establishing the temperature at which the equilibrium vapor over the pure metal in a suitable cell absorbs a specific resonance line of the metal atom. Then, the temperature at which equilibrium vapor over the carbide gives equal absorption was determined.

When this information is extrapolated to a common temperature, the free energy of formation of the carbide is calculated directly from the ratio of vapor pressures over the two phases.

This method assumes that the carbide phase dissolves little or no excess carbon, that graphite dissolves little or no metal carbide, and that no more carbon rich compound other than the equimolar carbide exists at the temperature of the measurements. These assumptions are most probably justified considering what is known about the phase diagram of this class of carbides[1].

II. EXPERIMENTAL APPARATUS

The apparatus and techniques used were essentially the same as described in earlier reports[2,3]. The construction of the cell and the few changes which proved necessary in this work are the only facts given here.

A. HOLLOW CATHODE DISCHARGE TUBE

The line spectrum of titanium and of zirconium was obtained by slipping a cup made from thin sheets of these metals in the bottom cup of the hollow cathode. Obtaining a stable discharge presented no problem in the case of titanium, but was rather difficult for zirconium. Occasionally the discharge had to be run for several days before the discharge would maintain itself in the zirconium cup under the usual current and gas pressure conditions. Once it started to operate properly, however, no further trouble was encountered for several days or weeks. This difficulty may have been due to the presence of an oxide coating on the metal but this was never proved conclusively.

The current was held at 30 m.a. and the argon pressure was 0.5 to 0.7 mm of mercury in all the runs used.

B. CELL DESIGN

The material under examination was placed in a graphite cell consisting of an 8" long graphite cylinder, having an outer diameter of 1 1/4" and a wall thickness of 1/8". At the two ends of the cell, tight fitting graphite diaphragms provided with an outside flange were slipped in and held in

position with graphite pins.

To study the absorption due to the vapor of the metal, a metal tube whose outside diameter was machined to precisely the same dimension of the internal diameter of the graphite cell was slipped into the cell. Flat metal sheet was then cut into a circle of the same dimension and slipped over the ends of the metal tube, and the graphite diaphragms were then pinned in place.

The diaphragms and the flat sheet metal liner had 1/4" or 3/8" holes drilled through their centers. Thus, after assembly, the cell consisted of an area completely lined with the metal under investigation, and the only openings were the holes which defined the optical path.

To study the equilibrium vapor over the carbide phase, the loose, powdered carbide (approximately 5-10 gms), was placed directly in the graphite cell and the graphite diaphragms were placed at the ends. Here the presence of a pure graphite surface insured that the partial pressure of carbon over the carbide was the equilibrium vapor pressure of carbon.

C. MATERIALS SAMPLES

The titanium carbide sample was provided by Union Carbide, and had an analysis of:

Titanium	80.2%
Total Carbon	19.5%
Free Carbon	0.01%
Oxygen	0.10%

and had undetermined, but very low, amounts of other impurities.

The titanium metal liners of the diaphragms consisted of C.P. Titanium sheet provided by the American Titanium Corp., and had an analysis of:

99.6% Ti	-	minimum
0.08% C	-	maximum
0.05% N	-	maximum
0.015% H_2	-	maximum
0.12% Fe	-	maximum

The titanium metal tube was made of A-40, #1 temper tubing provided by the Frasse Co.. Impurity limits for these tubes were:

0.10%	max.	Silicon
0.25%	max.	Iron
0.15%	max.	Manganese
0.10%	max.	Carbon
0.10%	max.	Aluminum
0.60%	max.	all other elements

The zirconium metal tube was furnished by the Carborundum Metal Co., and was CP-3 Seamless tube, having the following major impurities:

0.08%	Iron
0.02%	Chronium
0.0125%	Aluminum
0.01%	all other metals

Two different samples of zirconium carbide were used in this work. One was manufactured by Kennametal Inc., and had a reported analysis of:

10.56%	total carbon
0.22%	free carbon
1.0%	Titanium
0.5%	Tungsten
0.5%	Hafnium
0.25%	Niobium
0.10%	Tantalum

Less than 0.1% of other elements was present.

Initial experiments were performed using this sample. Subsequent work was carried out on a sample having an analysis which indicated that less free zirconium metal was present. This latter sample was obtained from A. D. Mackay, and has been analyzed at the General Electric Co.

Although the zirconium carbide samples appeared to have somewhat uncertain compositions this should make little difference in the reported results.

D. LIGHT PATH

The only modification made in the experimental equipment used consisted

of adding more precisely positioned masks in order to eliminate radiation from the hot furnace walls. This modification was necessary because at the considerably higher temperatures used in these experiments the danger of saturating the photomultiplier with a D.C. signal from the furnace was greatly enhanced. The monochromator was therefore placed further from the furnace, so that an image of the center of the furnace was made in free space before the light entered the monochromator slit. Masks were then placed at precisely the focal points of the image of the two hot graphite diaphragms at the ends of the cell, and all radiation from the diaphragms was thus eliminated from the beam. The masks were carefully positioned by means of multiple rack and pinion devices mounted rigidly to the monochromator table, and they had apertures only slightly smaller than the size of the diaphragm image at its focal point.

E. TEMPERATURE MEASUREMENTS

All temperature measurements were made with a Pyro Micro Optical Pyrometer modified at this laboratory by substituting a standard one ohm resistor and a portable Leeds and Northrup potentiometer for the calibrated ammeter. It had been previously found that the calibration of the ammeter tended to change during the course of a few weeks, and that great care had to be exercised on dry winter days to avoid the presence of drift due to the formation of an electrostatic charge on the case of the ammeter.

A lamp calibrated at the National Bureau of Standards in October 1958 was noticed to be in poor agreement with a pyrometer also calibrated at

the NBS during the summer of 1960. After further checking our instruments with the standards used at the Leeds and Northrup Co. and with another newly calibrated lamp from the NBS, the deviation was determined to be due to the older standard lamp. Since the temperature standard used in this laboratory had previously been this older lamp, extensive recalibration of the pyrometers was necessary. The discrepancy between the two standards was 7° at 1000°C, and 15° at 2400°C.

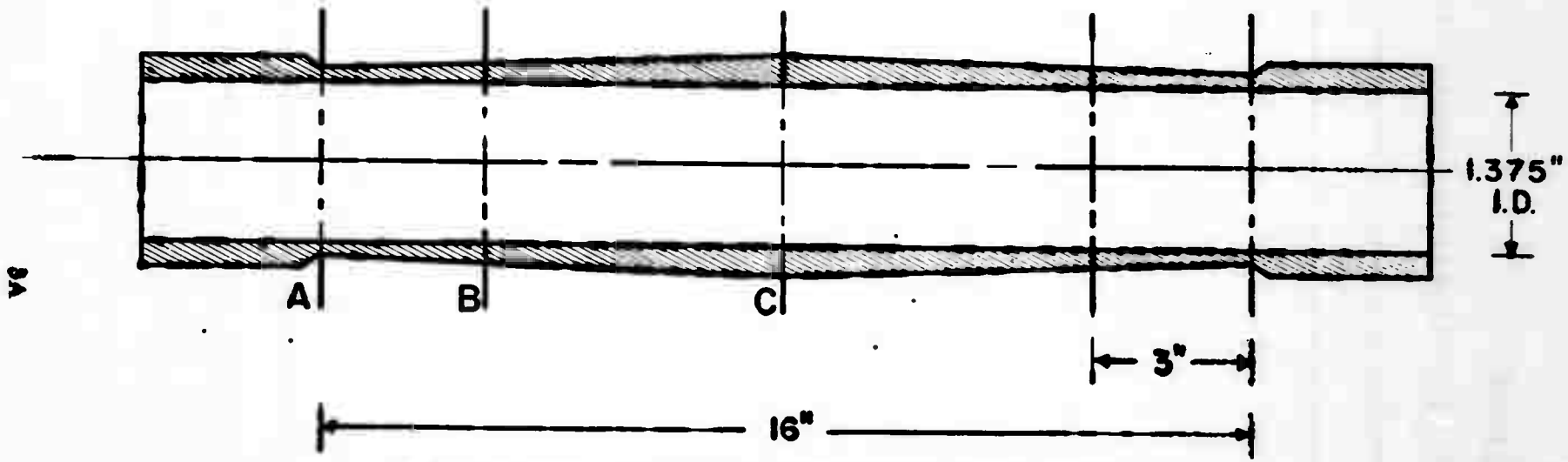
F. DIMENSIONS OF THE HEATER TUBES

The heater tubes used in this study are similar to those used previously. The dimensions of the three tubes used in obtaining the data used here are shown in Figure 1.

Since the presence of sizeable temperature gradients within the cell could not be avoided, a rather arbitrary way of deciding what to call the cell temperature had to be established. In order to test the accuracy of the averaging technique used, the study of the vapor over both zirconium and zirconium carbide was carried out twice, using two tubes having widely different temperature gradients. The accuracy of the averaging technique used can then be established by examining the relation between I/I_o and T for the two cases.

The dimensions of the two tubes used for this purpose are also given in Figure 1.

HEATER TUBE DIMENSIONS AS USED IN Ti C AND Zr C



	WALL THICKNESS AT: (in inches)			HEATER TUBE O.D. AT: (in inches)		
	A	B	C	A	B	C
Ti C	.040	.062	.100	1.455	1.499	1.575
Zr C #1	.040	.062	.100	1.455	1.499	1.575
Zr C #2	.048	.059	.100	1.471	1.493	1.575

Figure 1

III. EXPERIMENTAL PROCEDURE

A. ATOMIC LINES USED FOR ABSORPTION MEASUREMENTS

The resonance line chosen for measuring the absorption due to titanium atoms is the 3371.45A line due to an $a^3F_4 - y^3G_5$ resonance transition which promotes an electron from the 4s state to 4p. This line is known to have a relatively high oscillator strength, and it proved to be quite satisfactory for these studies.

Zirconium has the same outer electron configuration, and its spectrum bears a close resemblance to that of titanium atoms because both obey the L-S coupling rules to a high degree of approximation. The analogous zirconium line 3601.19A line was used, which has the same term designation and which results from the promotion of a 5s electron to 5p.

These lines also have the advantage of being far enough in the violet to be well removed from the peak of the black body curve for the temperature of the furnace, where difficulties due to photomultiplier saturation are most serious. Also, they are not so far in the violet to present problems due to loss of intensity or difficulties in obtaining transparent materials for windows.

The intensity of both lines in the hollow cathode discharge was quite adequate at the relatively low value of the current of 30 m. a.

B. EXPERIMENTAL PROCEDURE FOLLOWED

After starting the hollow cathode source, the carbon resistor furnace, containing a new AUC graphite heater tube and an empty graphite cell at the center of the tube, was heated to approximately 2000°C in a good vacuum.

This initial heating was carried out in order to distill the volatile impurities from the graphite. The temperature was then raised to a value 100° to 200° higher than the final temperatures at which measurements would be made, and 10 to 20 cm of mercury pressure of argon was introduced into the furnace.

After turning on the chopper and phasing the amplifier, blank values of $\frac{I}{I_o}$ were obtained by comparing the strength of the desired line after passing through the hot cell (I), and then passing it through the rapidly cooled cell (I_o). Initially, an increase in the strength of the signal was often observed which was attributed to residual amounts of zirconium and titanium in the graphite. Further prolonged heating in a vacuum, however, did not eliminate this apparent absorption. Some argon lines from the discharge then also appeared to be absorbed, so that the low value of I could not be attributed to absorption by the atomic species in question. Investigation revealed that this apparent absorption could be eliminated by carefully masking the radiation from the hot furnace walls, and that it was caused by a loss of sensitivity of the photomultiplier detector due to its partial saturation.

When the $\frac{I}{I_o}$ ratio became unity, the furnace was turned off and the cell was carefully removed from the furnace and loaded. The cell was then replaced in the heater tube without changing the optical alignment. The furnace was evacuated, a known pressure of argon gas was added, the power was turned on, and the measurement of $\frac{I}{I_o}$ was carried out precisely as described in a previous report.

Measurements were made over a 10° to 50° temperature range, and at several argon pressures in order to establish the effect of pressure

broadening. The temperatures were chosen so as to yield $\frac{I}{I_o}$ values of approximately 0.5.

C. PREPARATION OF SAMPLES

The preparation of samples presented some problems. General observation showed that initially the density of the metal species under investigation tended to be low and erratic. Prolonged heating of the samples tended to increase the absorption and greatly improved their reproducibility. This effect is attributed to the presence of a layer of oxide or of some other compound on the surface, which slows the rate of vaporization of the material and so tends to keep the atom density below the equilibrium value.

In the case of titanium metal and titanium carbide, this effect gave rise to no major difficulties, because heating in a vacuum at a temperature only one or two hundred degrees higher than the measurement temperature resulted in a rapid cleaning of the surface well before the melting point was reached. The considerable volatility of TiO_2 is probably responsible for this.

More difficulty was encountered in the case of zirconium metal and zirconium carbide. The zirconium carbide samples gave erratic results even after prolonged heating at 2700°C, and improvement was obtained only when the carbide sample was mixed intimately with a large excess of powdered pure graphite (National Graphite purest grade). Thus, physical contact with carbon appeared to be necessary in order to accomplish the removal of the surface film. The higher zirconium atom density shows that the change in density could not have been due to a change in the composition

of the carbide phase, since addition of carbon should have resulted in a lowering of the zirconium atom vapor pressure. When the graphite was added, the $\frac{I}{I_o}$ measurements readily settled to a reproducible value, and the excessive scatter disappeared. The data obtained is therefore considered reliable.

A different problem was encountered in the case of zirconium metal. Its low melting point (1857°C) was the maximum temperature to which the cell could be heated, and at this temperature rather long (1-3 hrs.) heating and pumping was necessary in order to clean the surface sufficiently. The melting of the zirconium had to be avoided, because the liquid tended to seep through the porous graphite cell walls and into the graphite heater tube. When this happened, large temperature gradients invariably were observed, due to the partial shorting of sections of the heater tube. Since the value of $\frac{I}{I_o}$ was approximately 0.60 at the melting point, care had to be taken to obtain sufficiently high absorption for good accuracy, while avoiding melting the metal.

D. TEMPERATURE MEASUREMENTS

Establishing the temperature of the cell with sufficient accuracy turned out to be the most difficult problem encountered. After trying several methods of obtaining the temperature inside the cell, the following one was chosen. The cross section of the cell is shown in Figure 2. The temperature was measured at four places, indicated by the letters A, B, C and D. No other points could be viewed adequately with an optical pyrometer, in view of the requirement that the pyrometer lens be uniformly filled with light emanating from the point being sighted. The difference in the size of the

GRAPHITE CELL WITH LINER

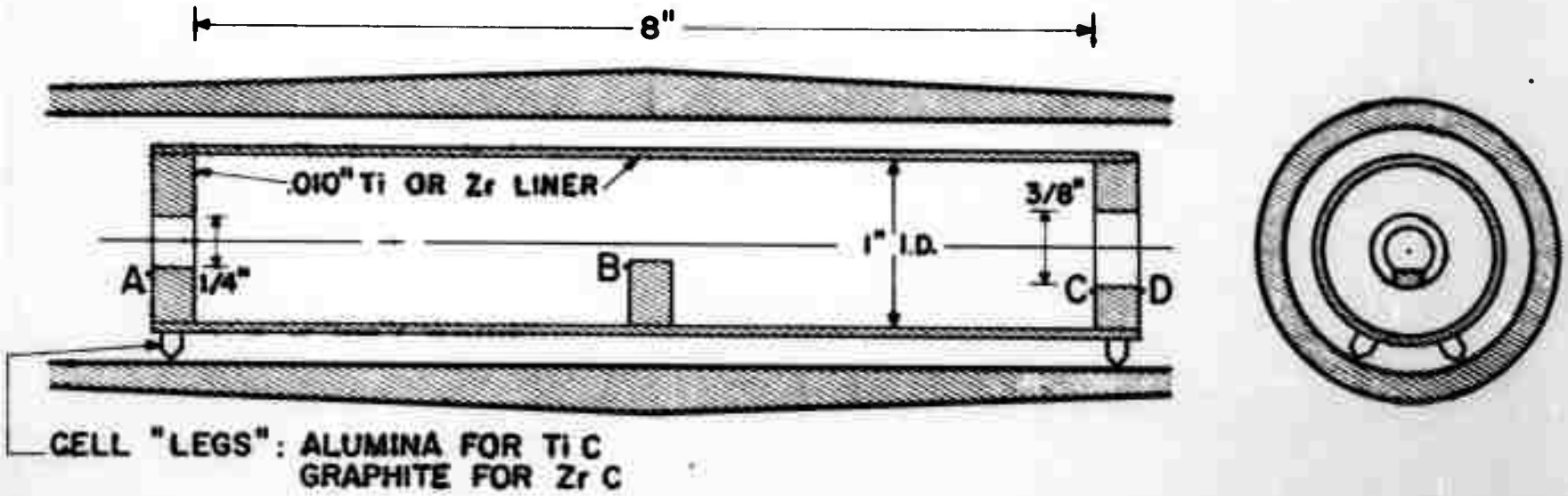


Figure 2

two holes through the diaphragms was necessary in order to obtain a reading on the inside of the other diaphragm.

The object indicated as (B) consisted of a piece of material sufficiently thick to be clearly visible in the optical pyrometer, but not so high that it blocked a large fraction of the light beam. When TiC and ZrC were under investigation, this object was a piece of graphite. When the vapor over the metal was being studied, (B) consisted of a bent piece of sheet of the metal used to line the cell.

Temperature measurements were made at the four indicated points both before and after each measurement of I. Preliminary work had shown that the temperature difference across the two diaphragms was almost identical. The temperature on the inside of the diaphragm shown on the left was therefore taken to be A + C - D. The average temperature of the two ends of the cell was then $\frac{A + 2C - D}{2}$, while the temperature of the center was B. The effective cell temperature was again assumed to be given by the average of $\frac{A + 2C - D}{2}$ and of B. Thus

$$T_{eff} = \frac{A + 2C - D + 2B}{4}$$

The difference between the center temperature B and the average temperature of the inside of the diaphragm is taken as a measure of the lack of uniformity of temperature of the cell, and is later listed as Δ.

$$\Delta = B - \frac{A}{2} - C + \frac{D}{2}$$

All of the listed values of A, B, C, and D are the average of the measurements taken before and after the measurement of the beam intensity I.

All recorded temperature readings were corrected for effects due to losses at the window and mirror.

IV. EXPERIMENTAL DATA AND METHODS OF COMPUTATION

A. EXPERIMENTAL DATA

The results obtained in the final sets of runs, after the many difficulties mentioned earlier were eliminated, are given in Tables I and II.

In order to determine the value of the free energy of formation of the carbides, the following questions must be considered:

1. How does the vapor pressure of the metal vary with temperature in the temperature interval of interest,
2. How does the value of the absorption coefficient vary with temperature and with the pressure of inert gas, and
3. What fraction of the metal atoms are in the electronic state capable of absorbing the resonance radiation used.

B. TEMPERATURE DEPENDENCE OF THE VAPOR PRESSURE OF ZIRCONIUM METAL

Reliable vapor pressure measurements on solid zirconium metal have been carried out at temperatures between 1949° and 2054°K. From these the temperature dependence of the vapor pressure can be calculated precisely from 1800°K up to the melting point of zirconium (2125°K) by:

$$\frac{d \ln P}{dT} = \frac{143,600}{RT^2}$$

Above 2125°K, the slope of the $\ln P$ vs. $1/T$ curve is changed by the heat of melting of the metal. Although no experimental value of the latter is available, it has been estimated to be 4000 cal/mole. From 2125° to 2700°K

TABLE I

Material	Run No.	Temperature (°K) A	B	C	D	T_{eff}	Δ	I/I_o	P_{Argon}(cm)
Tic	1	2164	2229	2207	2170	2217	25	.536	18.2
	2	2182	2247	2221	2188	2233	29	.426	18.9
	3	2170	2236	2210	2179	2221	30	.486	18.0
	4	2165	2231	2204	2173	2216	31	.509	18.3
	5	2166	2235	2206	2176	2218	34	.513	18.5
Ti	1	1625	1657	1652	1628	1654	6	.392	15.7
	2	1611	1645	1645	1611	1644	1	.541	15.5
	3	1614	1647	1647	1618	1646	2	.497	15.5
	4	1612	1645	1645	1616	1644	2	.561	15.3
	5	1613	1645	1645	1616	1644	2	.507	15.5
	6	1618	1651	1651	1621	1650	1	.449	15.1

TABLE II

Material and Tube	Run No.	Temperature (°K) A	B	C	D	T_{eff}	Δ	I/I_o	P_{Argon}(cm)
ZrC	1	2642	2801	2709	2659	2751	100	.582	17.6
heater	2	2642	2791	2706	2646	2748	87	.571	17.8
tube (1)	3	2647	2796	2705	2651	2750	93	.572	17.9
	4	2644	2787	2697	2644	2742	90	.591	17.9
ZrC	5	2682	2746	2711	2685	2728	36	.649	19.3
heater	6	2684	2752	2725	2694	2736	32	.646	18.0
tube (2)	7	2707	2773	2747	2718	2757	32	.599	18.1
	8	2700	2763	2740	2724	2746	35	.628	18.0
Zr	1	2067	2114	2108	2099	2100	22	.647	14.6
heater	2	2066	2112	2106	2100	2101	23	.678	15.2
tube (1)	3	2055	2100	2100	2091	2091	18	.733	15.1
	4	2048	2091	2091	2083	2089	17	.772	14.9
	5	2076	2116	2110	2100	2107	18	.652	14.8
Zr	6	2082	2062	2100	2106	2075	-26	.796	14.4
heater	7	2100	2074	2113	2119	2089	-28	.742	14.6
tube (2)	8	2096	2086	2126	2130	2098	-23	.728	14.9

the following equation will therefore be used:

$$\frac{d\,\ell n\,P}{dT} = \frac{139,600}{RT^2}$$

Similarly, the corresponding expression for the vapor pressure of titanium is

$$\frac{d\,\ell n\,P}{dT} = \frac{108,400}{RT^2}$$

up to the melting point (1950°), and becomes

$$\frac{d\,\ell n\,P}{dT} = \frac{103,800}{RT^2}$$

above the melting point, since the heat of melting has been estimated as 3,700 cal/mole.

C. VARIATION OF THE ABSORPTION COEFFICIENT WITH TEMPERATURE AND PRESSURE

While the effect of Doppler broadening is easily evaluated, correcting for pressure broadening and hyperfine structure of the line requires independent knowledge of the optical collision cross section and of the line structure. As was previously seen, these three effects interact in a complex manner. While the available data are insufficient to compute an oscillator strength from the absorption measurements given here, the calculation of the free energy of formation requires only an estimate of how the absorption coefficient varies over a short pressure and temperature interval. As shown here this estimate may be made with sufficient accuracy for our purposes.

(1) Hyperfine Structure

The isotopic composition of naturally occurring titanium and zirconium is given in Table III.

No information is available on the isotopic splitting or the hyperfine structure of the Ti 3371 A line. Notice however that almost 75% of the titanium consists of a single isotope having I = O, and consequently this line has no spectral hyperfine structure. Since the various isotopes may be assumed to have identical values of oscillator strengths, ignoring the existence of the other isotopes cannot lead to a change in the effective absorption coefficient of more than 25%. The effect on the measured $\frac{I}{I_o}$ is indeed probably considerably less than this, since the splitting may well be smaller than Doppler and pressure broadened width of the spectral line. Here, however, we are only concerned with the variation in the effective absorption coefficient on varying the temperature by approximately 500°. The effect of hyperfine structure will be seen to be probably quite small.

Zirconium also has five normally occurring isotopes. The most abundant has a mass number of 90, zero nuclear spin, and it makes up about half of naturally occurring zirconium. No hyperfine structure data is available for the 3601 A line, but the magnitude of the isotope splitting of a large number of other lines has been measured, including many having the same lower state. These are listed in Table IV. Notice that all the isotopes except one have zero nuclear spin, and so have no hyperfine structure.

TABLE III

Element	Mass No.	Relative Abundance	Nuclear Spin
Ti	46	7.95%	0
	47	7.75	5/2
	48	73.45	0
	49	5.51	7/2
	50	5.34	0
Zr	90	51.46	0
	91	11.23	5/2
	92	17.11	0
	94	17.40	0
	96	2.80	0

TABLE IV

Line (A)	Lower State	Upper State	=91	=92	=94	=96
6143	$^3F_2$	$^3F_2^o$		-8.5	-14.7	
6135	$^3F_3$	$^3F_3^o$		-8.7	-15.4	
6127	$^3F_4$	$^3F_4^o$		-8.8	-16.5	
5935	$^3F_2$	$^3F_3^o$		-11.1	-17.5	
5798	$^3F_3$	$^3D_2^o$	-3.7	-7.3	-14.4	-20.7
5736	$^3F_2$	$^3D_2^o$		-9.5	-16.3	
4688	$^3F_4$	$^3G_5^o$		-11.6	-21.0	
4635	$^3F_3$	$^3G_4^o$		-10.5	-18.5	
4576	$^3F_2$	$^3G_3^o$		-12.2	-16.2	

Since the Doppler halfwidth of the Zirconium 3601 A line is about 100×10^{-3} cm^{-1} at 2000°K the hyperfine structure will not appreciably affect the shape of the line.

Therefore, this hyperfine structure is ignored in both cases.

(2) Pressure Broadening

The optical collision cross section for the transitions in question with respect to collisions with argon gas are not known. Thus, in order to estimate the effect of pressure broadening, the dependence of $\frac{I}{I_o}$ on pressure has been measured directly while the cell temperature was kept constant.

Table V shows the results of these measurements. No apparent change is seen in $\frac{I}{I_o}$ for titanium on varying the argon pressure from 9 to 36 cm of mercury. Instead, an appreciable effect is seen in the case of zirconium, as might be expected in view of the greater size and polarizability of zirconium, but even in this case the Doppler broadening is greater than pressure broadening.

Thus, comparing the absorption over zirconium metal and over zirconium carbide, sufficient data can be obtained under conditions of equal number of collisions per second with inert gas. Since the number of collisions is proportional to the atom density P/T and also to the average velocity, and so to $T^{1/2}$, values of $\frac{I}{I_o}$ obtained at constant $PT^{-1/2}$ must be compared. The effect of pressure broadening is then cancelled to a good degree of approximation.

TABLE V

Run No.	Compound	Argon Pressure (cm of Hg)	$\frac{I}{I_o}$	$-\log \frac{I}{I_o}$
	TiC	18.5	.555	.256
		18.1	.531	.275
		18.5	.555	.256
		9.3	.549	.260
		9.3	.544	.264
		36.6	.555	.256
		36.5	.563	.250
	ZrC	18.8	.482	.317
		9.4	.419	.378
		9.2	.419	.378
		9.3	.402	.396
		37.5	.513	.290
		19.9	.484	.315
		36.5	.526	.280
		36.5	.517	.287
Ave.	TiC	9.3		.262
		18.4		.262
		36.6		.253
	ZrC	9.3		.384
		19.4		.316
		36.8		.286

The data given in Table III are not sufficiently precise to enable one to calculate an optical collision cross section, particularly in view of possible changes in effective path length with inert gas pressure.

(3) Doppler Broadening

In the absence of other broadening phenomena, a rise in temperature results in a change in the absorption coefficient at the center of the line (k_o) due to the increased Doppler broadening. An earlier report mentioned that k_o varies inversely as the square root of the temperature.

Thus, on going from 2000° to 2700°K, the value of k_o would be lowered by 16%. In the case of titanium, where pressure broadening and hyperfine structure have a negligible influence, the line is assumed Doppler shaped, and the temperature correction is surely applicable.

In the case of Zirconium, where pressure broadening is not negligible, the line is not Doppler shaped, and it is clear that the value of the absorption coefficient at the center of the line ($k_\nu - \nu_o$) must vary more slowly with temperature. While it could be argued that the correction should be 10-12% instead of 16%, the latter value is used anyhow, and no provision is made for the effect of pressure broadening other than the previously mentioned consideration of comparing $\frac{I}{I_o}$ values obtained at equal $PT^{-1/2}$.

(4) Line Shape from Hollow Cathode Source

The assumption has been made here, as was done previously, that the line from the hollow cathode source is thin compared to the line contour of the hot gas in the furnace. Appendix I gives the evidence which supports this assumption, and which has been collected during the course of these studies.

D. DATA REDUCTION

If the line is Doppler shaped, the partial pressure of atoms in the lower electronic state of the transition being studied has been shown to be proportional to $T^{3/2} \log \frac{I}{I_o}$. The constant of proportionality contains several fundamental constants, the value of the oscillator strength, the length of the cell, and some correction factors, but is, to a good degree of approximation, independent of the inert gas pressure and the temperature for the systems under investigation, as long as $P_{Argon}\ T^{-1/2}$ is held constant. The following expression may then be written:

$$AP' = T^{3/2} \log \frac{I}{I_o}$$

The value of AP' is calculated for all the runs listed in Tables I and II in the following Table VI.

All the -AP' values for the various runs performed on a particular material must now be reduced to a common temperature, so that these relative pressures can be averaged and compared. This is done making use of the integrated equations given in Section IV B:

$$\log \frac{P_1}{P_2} = \frac{\Delta H\ (T_1 - T_2)}{2.303 \times R\, T_1 T_2}$$

The values of $\Delta H/2.303\ R$ and of the common reference temperature T_2 for the four vaporization reactions are:

	$\frac{\Delta H}{2.303R}$	T_2
Ti	23,790	1650
TiC	34,480	2220
Zr	31,350	2100
ZrC	41,140	2740

TABLE VI

Material	Run No.	T	$-\log \frac{I}{I_o}$	$-AP' \times 10^{-4}$
ZrC	1	2751	.2351	3.39
	2	2748	.2434	3.51
	3	2750	.2426	3.50
	4	2742	.2284	3.28
	5	2728	.1878	2.68
	6	2736	.1904	2.72
	7	2757	.2226	3.22
	8	2746	.2020	2.91
Zr	1	2100	.1891	1.820
	2	2101	.1688	1.626
	3	2091	.1349	1.290
	4	2089	.1124	1.073
	5	2107	.1858	1.797
	6	2075	.0991	.937
	7	2089	.1296	1.238
	8	2098	.1379	1.325
TiC	1	2217	.2708	2.83
	2	2233	.3706	3.91
	3	2221	.3134	3.28
	4	2216	.2933	3.06
	5	2218	.2899	3.03
Ti	1	1654	.4067	2.74
	2	1644	.2668	1.78
	3	1646	.3036	2.03
	4	1644	.2916	1.94
	5	1644	.2950	1.97
	6	1650	.3478	2.33

In view of the shortness of the extrapolation, any uncertainty in the value of ΔH does not lead to errors worth mentioning.

The values of $-AP'$ reduced to these common temperatures are given in Table VII.

The AP' values given in Table VII are then averaged, and the root mean squares and root mean square deviations are given in Table VIII.

Finally, AP' must be converted to AP, where P is the total pressure of the metal atom under investigation rather than the partial pressure of atoms in the particular state capable of absorbing the radiation from the source. This is done by evaluating

$$N_1(T) = \frac{(2J_1 + 1)\, e^{-E_1/kT}}{\sum_i (2J_i + 1)\, e^{-E_i/kT}}$$

where the summation over i is the summation over all the states listed in reference 4 for the atomic species, and where the subscript 1 stands for the lowest $^3F_4$ level, which is the lower state of the transitions in question. Values of $N_1(T)$ are given for both titanium and for zirconium at the temperatures where measurements were carried out. These appear in Table IX.

Now, since $P' = N_1 P$, the quantity AP is easily calculated:

Material	T	$-(AP)_{Ave}$
Ti	1650	6.16×10^4
TiC	2220	8.47×10^4
Zr	2100	5.94×10^4
ZrC	2740	11.76×10^4

TABLE VII

Material	Run No.	T_1	$\frac{(T_1 - T_2)\Delta H}{T_1 - T_2 \times 2.303R}$	$-(AP')_{T_2} \times 10^{-4}$
ZrC	1	2751	.060	3.00
	2	2748	.044	3.16
	3	2750	.055	3.07
	4	2742	.011	3.18
	5	2728	-.066	3.11
	6	2736	-.022	2.86
	7	2757	.093	2.60
	8	2746	.033	2.98
Zr	1	2100	-	1.82
	2	2101	.007	1.59
	3	2091	-.064	1.50
	4	2089	-.079	1.29
	5	2107	.050	1.59
	6	2075	-.180	1.41
	7	2089	-.079	1.49
	8	2098	-.014	1.36
TiC	1	2217	-.021	2.97
	2	2233	.090	3.18
	3	2221	.007	3.22
	4	2216	-.028	3.27
	5	2218	-.014	3.12
Ti	1	1654	.035	2.54
	2	1644	-.053	2.01
	3	1646	-.035	2.19
	4	1644	-.053	2.19
	5	1644	-.053	2.23
	6	1650	-	2.33

TABLE VIII

Material	$(-AP')_{Ave} \times 10^{-4}$	T_2	rms dev.	rms dev. %
Ti	2.25	1650	0.13	5.8
TiC	3.15	2220	0.10	3.2
Zr	1.51	2100	0.15	9.9
ZrC	3.00	2740	0.18	6.0

TABLE IX

Atomic Species	$T^{o}K$	N_1
Ti	1650	.365
Ti	2220	.372
Zr	2100	.254
Zr	2740	.255

By making use of the expressions for the temperature dependence of the vapor pressure over the pure metal phases, the vapor pressure of Zr(g) over the ZrC(s) + C(s) invariant point at 2740° can be shown to be equal to the vapor pressure of Zr(g) over Zr(s) at 2144°. Similarly, the pressure of Ti(g) over TiC(s) + C(s) at 2220° is equal to the pressure over Ti(s) at 1666°.

These conclusions are the direct experimental information obtained by these experiments. No thermodynamic data has been used to this point except for the expressions for the temperature dependence of the vapor pressure over the metal. No detectable error could have been introduced by their use because of the shortness of the temperature extrapolations.

Other thermodynamic quantities are calculated in the succeeding section. Since these are obtained by making use of other thermodynamic data available in the literature, they are derived thermodynamic quantities.

E. EXPERIMENTAL ERROR

A relatively complete discussion of the sources of experimental error has been given elsewhere. The principal source of error is the experimental scatter of the measured values of $\frac{I}{I_o}$. The standard deviation of $\log \frac{I}{I_o}$, and thus of the pressure, was less than 6% for titanium and less than 10% for zirconium. This leads to an uncertainty of 0.3 kcal/mole in the calculated heats and free energies of TiC, and of 0.6 kcal/mole in the case of ZrC.

Uncertainties in the temperature readings and errors due to the temperature gradient are not important. This can be demonstrated by comparing the values of $(-\Delta P')_{T_2}$ (which are corrected to a common temperature) obtained for Zr and ZrC using the two different heater tubes.

	Tube	Zr	ZrC
rms value of $-(\Delta P')_{T_2} \times 10^{-4}$	1	1.57	3.10
	2	1.42	2.89
rms deviation on separate sets	1	.17	.07
	2	.05	.19
difference in rms values of $-(\Delta P')_{T_2} \times 10^{-4}$		.15	.21

In this table is seen that the difference between rms values obtained from the two tubes is approximately the same as the rms deviation of values obtained on a single tube. Notice that the gradient is quite different for the two tubes used (Δ differs by 50°), and that Δ is strongly dependent on the temperature.

In view of these findings the decision was made to use the averaged data from both tubes rather than trying to select data obtained in runs where the temperature gradient is smaller. The probable error of the reported results is felt to be of the order of the root mean square deviations reported in the preceding paragraph.

The claimed accuracy is somewhat more conservative, and is ± 0.5 kcal for TiC and ± 1 kcal for ZrC for free energy and enthalpy values.

V. CALCULATION OF DERIVED THERMODYNAMIC QUANTITIES

The directly obtained thermodynamic data consists of a statement that the pressure of metal atoms is equal over the pure metal and over the carbide at two specified temperatures. This must now be stated in terms of more customary thermodynamic quantities.

A. ΔF_T^o of MC(s) = M(g) + C(s)

The standard molar free energy change for this reaction may be easily calculated making use of literature data. The only quantity needed is the vapor pressure of metal atoms over the metal at a temperature where particularly reliable experimental information is available.

From reference 5, the following vapor pressures are obtained:

$T = 2144^o \quad \log P_{Zr} = -7.660$

$T = 1666^o \quad \log P_{Ti} = -7.296$

For the vaporization reaction:

$$MC(s) = C(s) + M(g) \qquad (1)$$

$$\Delta F_T^o = -RT \ln P_M$$

But, for

$M = Zr$, at $T = 2740 \quad \log P_{Zr} = -7.660$

and for

$M = Ti$, at $T = 2220 \quad \log P_{Ti} = -7.296$

so that

ΔF^o_{2220} (TiC) = 74,130 kcal/mole

ΔF^o_{2740} (ZrC) = 96,060 kcal/mole

B. ΔF°_{ft} - STANDARD MOLAR FREE ENERGY OF FORMATION

The standard molar free energy of formation of the carbides in question is, by definition, the free energy change of the reaction

$$M(s) + C(s) = MC(s)$$

This reaction may be considered to be the result of subtracting reaction (2) from (3).

$$M(s) = M(g) \qquad (2)$$

$$MC(s) = M(g) + C(s) \qquad (3)$$

Values of ΔF°_{T} for reaction (3) have just been obtained above, while those for reaction (2) are given in reference 5.

$$\Delta F^{\circ}_{2220}\,(Ti)\,(\ell) = 38,660 \text{ kcal/mole}$$

$$\Delta F^{\circ}_{2740}\,(Zr)\,(\ell) = 57,300 \text{ kcal/mole}$$

Then

$$\Delta F^{\circ}_{f_{2220}}\,(TiC) = -35.470 \text{ kcal/mole}$$

$$\Delta F^{\circ}_{f_{2740}}\,(ZrC) = -38.760 \text{ kcal/mole}$$

These free energy values depend on the magnitude of the heat of melting of the pure metal, and on the heat capacity of the liquid at temperatures as much as 600° above the melting point. No reliable experimental data are available for these quantities, so that the value of ΔF°_{T} (M) in reference 5 is based in part on their estimated value in both metals. While no reliable quantitative estimate can be made of the resulting error, our opinion is that it is smaller than the uncertainty due to experimental errors.

C. ΔH°_{f298} of TiC

It is interesting to compare literature values of the above quantities with the free energy of formation of TiC given above. In this case sufficient data are available for a complete comparison of the compatibility. The heat of formation at $0^{\circ}K$ of TiC is given by

$$\Delta H^{\circ}_0 = \Delta F^{\circ}_{f2220}(TiC) + (F^{\circ}_{2200} - H^{\circ}_0)_{Ti(s)} + (F^{\circ}_{2200} - H^{\circ}_0)_{C(s)} - (F^{\circ}_{2200} - H^{\circ}_0)_{TiC}$$

The values of the various quantities are given in the following table:

	Value Kcal/mole	Reference
ΔF°_{f2220}	-35.470	this report
$(F^{\circ}_{2220} - H^{\circ}_0)_{Ti(s),(\ell)}$	-33.920	6
$(F^{\circ}_{2220} - H^{\circ}_0)_{C(s)}$	-12.970	6
$(F^{\circ}_{2220} - H^{\circ}_0)_{TiC(s)}$	39.930	6

so that

$$\Delta H^{\circ}_0 = -42.430 \text{ kcal/mole}$$

$$\Delta H^{\circ}_{298} = -42.730 \text{ kcal/mole}$$

which is in good agreement with the most reliable value available[6]:

$$\Delta H^{\circ}_{298} = -43.8 \pm 2.0 \text{ kcal/mole}$$

This agreement supports the value obtained by Humphrey, and is further evidence that TiC does not tend to dissolve appreciably excess carbon even at $2220^{\circ}K$.

D. $\Delta H^{\circ}_{f_{298}}$ ZrC

A completely analogous computation could be carried out for ZrC, however, sufficient thermodynamic data are lacking in order to do this. An approximation has been made for the heat capacity of ZrC from 298° to 1700°K by Krikorian[7] as follows:

$$Cp = 11.06 + 1.52 \times 10^{-3} T - \frac{2.43 \times 10^{5}}{T^{2}}$$

From this expression and the enthalpy and entropy values for Zr(s) and C(s) given in reference 5, the change in the entropy and enthalpy of formation from 298° to 1800° can be calculated. For lack of further information at temperatures above 1800°K the assumption is made that ΔH°_{f} and ΔS°_{f} are constant using the value of $\Delta S^{\circ}_{f_{298}} = -2.7 \pm 1$ e.u.[7]. The free energy of formation of ZrC at 2740°K can be written in terms of $\Delta H^{\circ}_{f_{298}}$ as follows:

$$\Delta F^{\circ}_{f_{2740}} = \Delta H^{\circ}_{f_{298}} + (H^{\circ}_{1700} - H^{\circ}_{298})_{ZrC} - (H^{\circ}_{1700} - H^{\circ}_{298})_{Zr(s)}$$
$$- (H^{\circ}_{1700} - H^{\circ}_{298})_{C(s)} - H_{Zr_{fusion}} - T\left[\Delta S_{f_{298}} + (S^{\circ}_{1700} - S^{\circ}_{298})_{ZrC}\right.$$
$$\left. - (S^{\circ}_{1700} - S^{\circ}_{298})_{Zr(s)} - (S^{\circ}_{1700} - S^{\circ}_{298})_{C(s)} - \frac{H_{Zr_{fusion}}}{2125^{\circ}}\right]$$

Therefore,

$$\Delta H^{\circ}_{f_{298}} = -38.76 + .83 + 4.0 + 2.740\left(-2.7 - .41 - \frac{4000}{2125}\right)$$

$$\Delta H^{\circ}_{f_{298}} = -47.6 \pm 3 \text{ kcal/mole}$$

The error of ± 3 kcal/mole is assigned on the basis of the estimated error of ± 1 e.u. in the entropy of formation. This value of the heat of formation of ZrC is in agreement with the value given by Krikorian[7] of -44.4 ± 1.1 kcal/mole. When a more reliable entropy value becomes available, $\Delta H^{\circ}_{f_{298}}$ of ZrC can be calculated to a precision inherent in the $\Delta F^{\circ}_{f_{2740}}$, namely ± 1 kcal/mole.

Alternately, if it is assumed that the value of the heat of formation at 298°K as given by Krikorian is substantially correct, ΔS^{o}_{298} can be calculated from the above data. This leads to a value for ΔS^{o}_{298} for ZrC of 1.9 ± .8 c.u.

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APPENDIX A

SHAPE OF LINE FROM HOLLOW CATHODE SOURCE

I. Introduction

Previous reports in this series describe how absorption measurements of resonance lines have been used to determine the vapor pressure and heat of formation of some compounds or the value of the oscillator strength of atomic resonance lines. In this method, a sharp line is generated in a hollow cathode discharge tube, and its absorption by the hot equilibrium vapor is measured using suitable spectrophotometric equipment. The calculations for converting the measured absorption to the oscillator strength, or to vapor pressure have been made assuming that the line from discharge source is infinitely thin compared to the absorption line width.

Direct measurements of the line contour and half width would provide the most conclusive information. They would require the detailed examination of the lines with an interferometer having a resolving power of 2×10^6. Such measurements require elaborate instrumentation, and are very time consuming. They have not been undertaken, since it is hoped that the following considerations will establish indirectly that the thin line assumption is satisfactory.

This appendix summarizes the evidence that has been obtained regarding the shape of the line from the source. Three arguments are advanced to show that the thin line assumption is very probably correct; they are:

1) The method of operation of the source tends to minimize the magnitude of Stark, pressure and Doppler broadening, and of line reabsorption.

2) Measurements of $\frac{I}{I_o}$ as a function of lamp current show no drop in absorption at higher currents. This indicates that Stark broadening and reabsorption do not affect the results obtained.

3) Measurement of the density of sodium vapor in equilibrium with sodium metal yields results which agree with more precise information found in the literature.

II. Experimental Equipment and Source Operation

The experimental source used in these studies has been described in a previous report, and is shown in Figs. 1 and 2.

The hollow cathode was patterned after the one described by Tolansky. It consists of a copper cathode cup region at the bottom, a ring anode made of nickel placed above it, and a vacuum tight glass envelope provided with a window at the top and with inlet and outlet tubes for the carrier gas. This design is most convenient when one desires to operate the discharge at a low temperature; the whole tube is then lowered in a refrigerant bath, leaving only the top part of the glass envelope and the window exposed. All the work carried out here has been performed with the cathode immersed in liquid nitrogen.

Constant line intensity can be obtained only if the liquid nitrogen level is held quite constant. An automatic constant level filler is therefore used to replenish the liquid nitrogen.

The discharge is operated in argon carrier gas at a pressure of 0.3 to 0.6 mm. of mercury as measured by a Pirani gauge. At this pressure the

discharge tended to remain in the cup and was most stable. The argon gas used was a 99.97% pure Air Reduction Co. product, which was further purified before introducing it into the discharge tube by passing it over hot titanium turnings and through a liquid nitrogen trap. This purified argon was introduced into the top of the discharge tube through a needle valve, and was removed from the cathode cup by continuous pumping with a small diffusion pump.

The flow velocity under typical operating conditions is maintained at approximately 150 ml/sec. This high value was chosen in order to avoid the formation of a cloud of sputtered material in the area above the hollow cathode cup, because this cloud is the cause of possible reabsorption of the generated spectral lines.

The current through the discharge is controlled by varying the voltage generated in a 300 m.a., 500 volt DC source and by placing a 6000 ohm resistor in series with the discharge tube.

All of the lines used in the studies described in previous reports were very intense resonance lines. The intensity of these lines was sufficient even at the lowest currents which would support a stable discharge; these varied from 12 m.a. to 30 m.a. depending on the composition of the cup line and on the element under investigation. Currents only slightly higher than this lower limit were used, because the intensity of these lines was noticed to vary rapidly with the current in this region. At higher currents the intensity is more constant, indicating that line reabsorption may be becoming

increasingly important. The observation that this drop in the rate of growth occurs at even higher currents for weaker lines confirms our interpretation of this effect.

Information available in the literature indicates that these conditions of operation tend to minimize line broadening, and that the line width so obtained is approximately what would be predicted for pure Doppler shapes for a temperature of 100°-300°K.

III. Dependence of Measured I/I_o on Source Current

The fact that the intensity of the lines is strongly dependent on the current density has already been mentioned. Most likely the concentration of atomic species is in the cathode region, and so the amount of reabsorption will also depend strongly on the current.

If reabsorption caused excessive line broadening, the value of $\frac{I}{I_o}$ will depend on the current even if everything else is held constant.

This dependence has been investigated in some detail for the case of the copper 3247 line and especially the zirconium 3601 line.

The relevant data are tabulated below:

Table I

Run No.		Lamp Current
78	0.31	30 m.a.
79	0.36	20
80	0.32	30
81	0.32	26
82	0.35	26
83	0.33	26
87	0.28	23
88	0.30	24
90	0.34	28
95	0.30	28
96	0.29	30
97	0.42	30
98	0.30	30
99	0.32	30

Although this variation in current changes the line intensity by more than a factor of two, no variation in $\frac{I}{I_o}$ can be attributed to the changing current.

Similarly, in the case of zirconium, the value of $\frac{I}{I_o}$ was measured as a function of current through the hollow cathode source. The furnace temperature and inert gas pressure were the same for all the runs listed, so any variation in $\frac{I}{I_o}$ can be attributed solely to a change in the line shape.

Table II

Current through Lamp m.a.	$\frac{I}{I_o}$	$-\log \frac{I}{I_o}$
30 m.a.	.443	.354
30	.439	.358
30	.432	.365
40	.448	.344
40	.422	.375
50	.413	.384
50	.432	.365
65	.445	.352
80	.409	.388

This remarkable constancy in $-\log \frac{I}{I_o}$ shows that the line width is not changed significantly even by operating lamp currents approximately three times as great as the normal operating value.

Clearly then, Stark broadening and line reversal do not affect the line shape sufficiently to render invalid the assumption that the emitted line is very thin.

IV. Test of Method with Sodium Vapor

The final evidence supporting the assumption that the lines are thin compared to those absorbed by the hot atoms in the furnace is based on the agreement between the measured vapor pressure of sodium and the best values given in the literature. In the case of sodium, good values of the vapor pressure, oscillator strength, hyperfine structure and pressure broadening constant are available. The good agreement therefore indicates that the assumptions which have been made are satisfactory, and that this method is capable of yielding satisfactory values for the vapor pressure. The demands on this method are fewer when it is used for measuring free energies of formation, since in this case errors tend to cancel almost completely.

Conclusions

A fairly safe assumption is that the line generated from a hollow cathode source operated as described above has a width typical of a Doppler shaped line for a temperature of approximately 100°-300°K. Such a width has been shown to introduce an error of approximately 10-15% in measured vapor pressures calculated assuming the line is infinitely thin.

When the method is used for measuring free energies of formation, the vapor pressure ratio obtained has a probable error of 5% or less due to this assumption.

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TECHNICAL INFORMATION SERIES

AUTHOR	SUBJECT CLASSIFICATION	NO.
G. L. Vidale	Thermodynamic Properties of Vapors	R61SD147
		DATE: August, 1961

TITLE: MEASUREMENT OF VAPOR PRESSURE OF ATOMIC SPECIES FROM SPECTROPHOTOMETRIC MEASUREMENTS OF ABSORPTION OF RESONANCE LINES

ABSTRACT: Spectrophotometric measurements of the absorption of the Ti_{3371} and the Zr_{3601} resonance lines were made of the equilibrium vapor over the pure metals and over the corresponding carbides, utilizing a hollow cathode discharge tube source to generate the thin resonance lines. From the ratio of the pressure of the metal atoms over the pure metal, and over TiC and ZrC, the standard free energy of formation of each carbide has been computed. The corresponding values of the standard heat of formation were then obtained.

It was found that for TiC

$$\Delta F^{o}_{f_{2220}} = -35.5 \pm .5 \text{ kcal/mole}$$

$$\Delta H^{o}_{f_{298}} = -42.7 \pm .5 \text{ kcal/mole}$$

and for ZrC

$$\Delta F^{o}_{f_{2740}} = -38.8 \pm 1 \text{ kcal/mole}$$

$$\Delta H^{o}_{f_{298}} = -47.6 \pm 3 \text{ kcal/mole}$$

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AUTHOR G. L. Vidale / M. J. Linevsky

COUNTERSIGNED Joseph Fabian

DIVISION Defense Electronics

LOCATION Valley Forge Space Technology Center, King of Prussia, Pa.